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Mechanical strength and corrosion detection of pozzolanic cement

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KEYWORDS

Blended cement hydration;
Electrical conductivity;
Steel reinforcement;
Corrosion detection

Abstract Various pozzolanic cement pastes based on ordinary Portland cement (OPC), granulated blast furnace slag (GBFS) and metakaolin (MK) were studied. Mixes were prepared using a water/solid ratio (W/S) of 0.25 wt.%. Hydration characteristics of the different hardened cement pastes were investigated via the examination of chemically-combined water content, compressive strength, and X-ray diffraction analysis under normal curing conditions at various time intervals up to 90 days. Thermal analysis (DTA/TGA) was carried out for the mix containing 30% Mk and GBFS at 28 days. The electrical conductivity was measured during the early stages of hydration for the various cement pastes at 30 °C. Moreover, the corrosion potential of reinforced steel embedded in the metakaolin–slag–cement system was studied in comparison to their corresponding ordinary Portland cement, to evaluate the probability of steel corrosion. The results showed that the values of Wn% in these blended pastes are higher than blended pastes with slag or metakaolin only. Also, mix containing 70% OPC, 15% Mk and 15% GBFS has higher compressive strength and corrosion resistance than the net cement paste. The results of thermal analysis indicate that the presence of 30% GBFS and MK consumed the CH formed as a result of the hydration of OPC (pozzolanic reaction).

Introduction

Pozzolanas are defined as materials which, though not cementitious in themselves, contain reactive silica and alumina in a finely divided form, which are capable to combine with lime at ordinary temperatures in the presence of water to form stable insoluble compounds possessing cementing properties.

The study suggested that the reactions of pozzolanic cements were slower than those of Portland cement, and silica fume reacts earlier than fly ash and slag [1,2]. The combined water content increases with increasing the amount of silica fume and decrease with increasing slag content [3]. Other studies [4] showed that the replacement of 20% cement with 12% silica fume and 8% clay increases the value of the compressive strength. These results indicate that appropriate use of silica fume and aluminosilicate clays may make cement-based materials stronger. Also, the presence of metakaolin (10%)

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in cement mortars increases the compressive strength and decreases the porosity values [5].

Jau and Tsay [6] used slag to substitute up to 50 wt.% of cement to make slag–cement mixes. The test results showed that the slag cement with 20–30% substitution has the best corrosion resistance. Silica fume (SF) and blast furnace slag (GBFS) at different ratios instead of Portland cement (PC) are used to improve the mechanical properties of concrete and to increase the corrosion resistance of steel embedded in concrete. It was observed that the samples with 10% SF + 20% BFS had the highest compressive strength, and that the mix samples with 10% SF + 40% BFS and 0.35 water-binder ratios had the lowest corrosion current density. As a result, it can be concluded that the mineral admixtures improved the compressive strength and corrosion current density [7]. The corrosion resistances of concrete containing granulated blast-furnace slag (GBFS) were studied [8]. It was suggested that much stronger corrosion resistance can be achieved, if higher volume of GBFS is added. The corrosion rate values of steel embedded in both fly ash and slag mixes [9] showed much lower values than the corresponding OPC mixes. The electrical response characteristics of setting pastes can be used as an effective means of studying the progress of cement hydration. It can also be used for monitoring structural changes occurring within the paste, as well as, reflecting the hydraulic reactivity of granulated slag and silica fume as pozzolanic constituents of the hardening pastes [10]. From these studies it is evident that fly ash and slag blended cements are better than those of the corresponding ordinary cements.

The objective of this investigation is to study the physico-chemical, mechanical characteristics and electrical conductivity of some blended cements with artificial pozzolana produced by using one of the industrial solid wastes (slag) and pozzolana (metakaolin). Also, the corrosion behavior of steel bars embedded in neat ordinary Portland cement (OPC) and in the presence of slag–metakaolin as a mineral admixture was determined.

Experimental

The materials used in this investigation were; ordinary Portland cement (OPC), granulated blast furnace slag (GBFS) and metakaolin (MK is kaolin ignited at 800 °C for 1 h). The chemical oxide composition of starting materials is given in Table 1. Based cement is referred to as: 100% OPC (Mo), 90% OPC + 5% GBFS + 5% MK (MI), 80% OPC + 10% GBFS + 10% MK (MII) and 70% OPC + 15% GBFS + 15% MK (MIII).

The water/solid ratio used was 0.25 for all mixes. The pastes were molded at 30 °C in the form of one inch cubic molds and cured under about 100% relative humidity for the first 1 day. The samples are then demolded and immersed under tap-water for the rest of the hydration times which extended up to 90 days.

The hydration characteristics of the different cement mixes were investigated via: (1) The determination of chemically-combined water content by determining the weight loss of the dried samples (at 100 °C) on ignition at 950 °C. (2) X-ray diffraction analysis by using a copper target under working conditions of 40 kilo, 25 milliampers and Nickel filter. (3) Compressive strength was carried out by using Ton industric type, West Gerrmany, and having a maximum load of 60 tons. (4) Determination of porosity of various mixes at 28 days hydration. (5) Thermal analysis (DTA/TGA) was carried out under dynamic flow of nitrogen (30 ml/min) and a heating rate of 10 °C/min using a Shimadzu TGA – 50 thermoanalyzer. Also, differential thermal analysis was carried out under a dynamic flow of nitrogen gas (30 ml/min) and a heating rate of 10 °C/min up to 900 °C, using a Shimadzu DTA-50. (6) Electrical conductivity. (7) Corrosion detection.

Chemically-combined water content (Wn%) *i*s calculated by taking about one gram of two representative samples of each dried hardened cement paste (dried at 100 °C for 24 h) that were weighed in silica crucibles and ignited for one hour at 950 °C, cooled in desiccators then weighed once more. The chemically combined water (i.e. the amount of water retained after drying) was calculated using the following Eq. (1):

$$\mathrm{Wn}(\%) = (W_2 - W_3)/(W_3 - W_1) \times 100 \quad (1)$$

where: W_1, is the weight of the empty crucible (g); W_2, the weight of the crucible + sample before ignition (g); and W_3, the weight of the crucible + sample after ignition.

Porosity measurement was carried out by using two representative cubes of each mix after 28 days of hydration; the average of the two results was considered, and applying the following Eq. (2):

$$P(\%) = \frac{(W_1 - W_3)}{(W_1 - W_2)} \times 100 \quad (2)$$

where: W_1, weight in air of saturated surface-dry cube; W_2, weight of cube suspended in water; W_3, weight of cube (in air) after drying at (100–105 °C) for 24 h.

The paste used for *conductivity measurements* was prepared by mixing the deionized water to exactly 10 g of sample by using the water/solid (W/S) ratio of 0.25. Mixing is continuously carried out for 3 min. The paste was transferred into a cylindrical plastic sample holder of 15 mm internal diameter, with stainless steel electrodes at both sides with 12 mm distance between them. Electrical conductance of each paste was measured at 30 °C at various time intervals from 5 min up to 24 h.

Half-cell potentials were measured, as a function of curing time, for all samples using a saturated calomel electrode (SCE) on a wet mortar surface directly above the steel electrodes. In all specimens, polished steel electrodes of 1 cm diameter and 4 cm long were used as working electrodes (Fig. 1). The specimens were subjected to potential monitoring after 1 day of

Table 1 Chemical oxide composition of starting materials, (wt.%).

Oxide (%)	SiO_2	Al_2O_3	F_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl	L.O.I
Material										
OPC	20.34	5.21	3.67	62.28	2.4	2.94	–	–	–	2.4
GBFS	36.9	10.6	1.65	34.3	8.52	0.60	0.83	0.48	0.015	–
Metakaolin	46.02	39.44	0.40	0.30	0.26	–	–	–	–	1.5

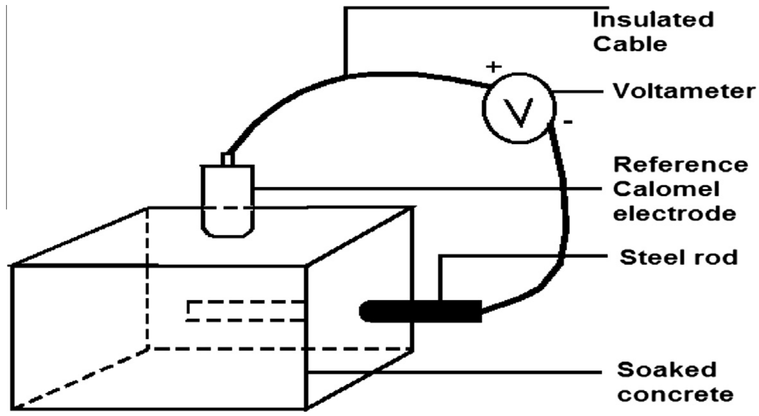

Fig. 1 Electrical conductivity cell.

hydration. To measure corrosion potential two sets of paste blocks, free and with different slag–metakaolin–cement pastes were made. The first set is aged in a humidity chamber at an average relative humidity (RH) $\approx$ 100% until 60 days after casting. The second set is partially immersed in 3.5% NaCl solution.

Results and discussion

Chemically combined water contents (Wn%)

The chemically-combined water contents (Wn%) for all hardened cement pastes increase gradually with hydration time as shown in Fig. 2. This is mainly due to the progress of hydration and precipitation of increasing amounts of the hydration products. It is evident from Fig. 2, that the partial replacement of OPC by metakaolin–slag caused a notable drop in the combined water contents for all blended cement pastes. Also, the blended cement paste containing 15% metakaolin and 15% slag mix (MIII) showed the lowest values of combined water content as compared with those of the other mixes at all ages of hydration. The values of Wn% in these blended pastes are higher than blended pastes with slag or metakaolin only. Such results are in a good agreement with previous studies [3].

Compressive strength

The compressive strength values of the hardened blended cement pastes increase with a hydration time up to 90 days as shown in Fig. 3. This is due to the increase in the amount of hydration products (CSH) which is responsible for binding. As the hydration proceeds, more hydration products (CSH) are formed and accumulated within the pore system of the hardened paste. Therefore, the porosity of the cement pastes decreases and then the compressive strength increases. The compressive strength values obtained for the hardened blended Portland cement paste (MI) is somewhat less than that of neat OPC paste at all ages of hydration up to 90 days. This result may be due to OPC substitution effect in this mix. Obviously, as metakaolin–slag content increases in cement blends of the other two mixes, (MII and MIII), the activity of the pozzolanic reaction with the release of free lime increases, hereby the strength drop is not only gradually diminished but also there is an increase in their values than OPC. This can be attributed to the two factors; reduce the porosity percent; (Mo; 32.29%, MII; 25.57% and MIII; 21.76%). In addition, the formation of additional amounts of CSH (binding agent) took place as a result of the pozzolanic reaction between metakaolin–slag and free lime released during Portland cement hydration. This also leads to continuous increase in the compressive strength with hydration time. Ultimately, the strength results indicated that the metakaolin–slag–cement blend of mixes (MII and MIII) represents the optimum constitution suitable for the production of pozzolanic cement made of local clays–slag. These results also indicate that appropriate use of slag and ignited metakaolin aluminosilicate clay may make stronger cement-based materials.

Phase composition

The XRD patterns of the hydration products formed after 90 days for all mixes are illustrated in Fig. 4. The CH peaks

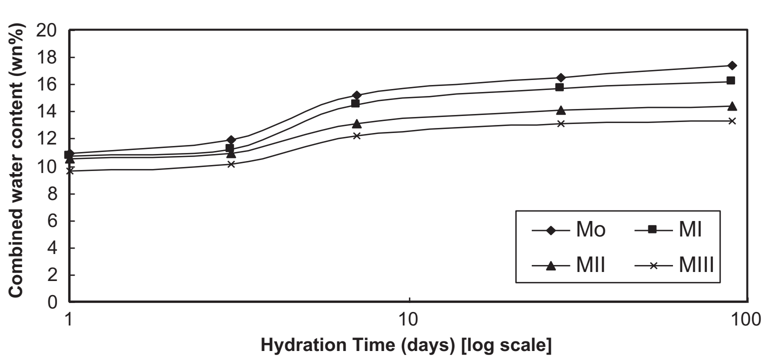

Fig. 2 Combined water contents of composite cement pastes as a function of time.

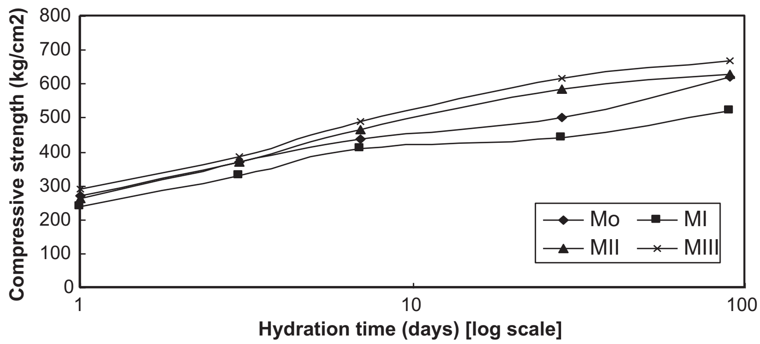

Fig. 3 Compressive strength of composite cement pastes versus hydration age.

at 4.9 and 2.62 Å decrease in intensity in the presence of MK and GBFS. As the percent of the additive increases, the intensity of CH decreases due to the reaction between CH and Mk and GBFS (Eqs. (3) and (4)).

$$\mathrm{CH} + \mathrm{MK} \rightarrow \mathrm{CSH} + \text{other products} \quad (3)$$

$$\mathrm{CH} + \mathrm{GBFS} \rightarrow \mathrm{CSH} + \text{other products} \quad (4)$$

The formed CSH phase accumulates in the pores, so increase of the compressive strength is observed.

Electrical conductance

The results of the conductivity time curves are illustrated in Fig. 5. The initial hydrolysis of the OPC constituents might be responsible for the increased conductivity values at the initial stages of hydration up to 36–48 min. The charge carriers are mainly Ca^{++}, OH^{-}, SO_4^{-} and alkali ions. The gradual decrease in the conductivity values after the peak maximum reflects the rapid consumption of ions as a result of the formation of cement hydration products, mainly as CSH. This observation is in a good agreement with previous study [11].

The lower intensity of the conductivity maxima observed for blended OPC pastes compared with that of the neat OPC paste is mainly related to the partial replacement of OPC by 10, 20 and 30 wt.% of metakaolin–slag. In addition, the conductograms of pastes become more steeper by increasing the amount of metakaolin–slag in the blends, a result which reflects the prompt pozzolanic reaction of metakaolin–slag with the released $Ca(OH)_2$ from the hydration of OPC fraction in the cement blends.

Thermal analysis

Thermal analysis techniques of differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) were used to obtain more information about qualitative and quantitative analysis of the mixes. Figs. 6 and 7 show DTA and TAG

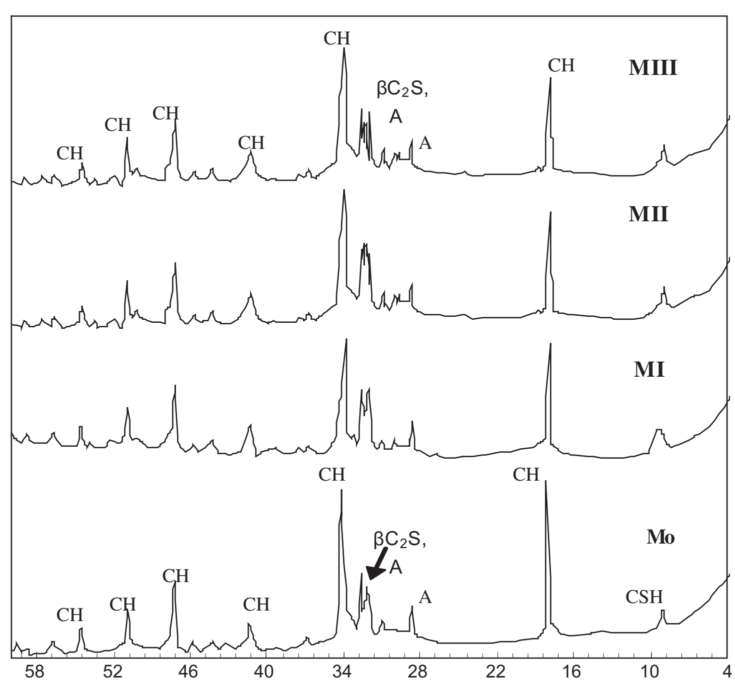

Fig. 4 XRD patterns of various cement pastes after 90 days of hydration. Where: CSH, calcium silicate hydrate; CH, calcium hydroxide; A, alite; and β-C_2S, β-Dicalcium silicate.

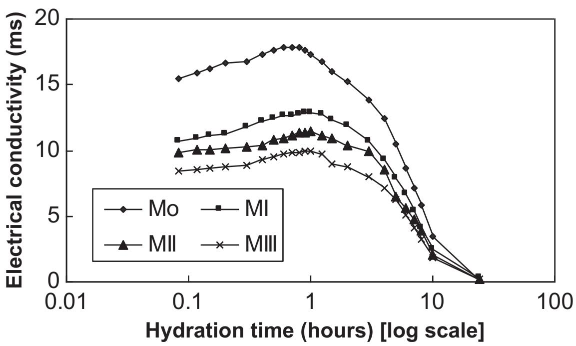

Fig. 5 Electrical conductivity-hydration time curves obtained as a function of mix composition.

curves of the control mix Mo and mix MIII which contains 30% GBFS and Mk (w/w) hydrated for 28 days. It can be noticed that the endothermic peaks in the DTA curves at 50–120 °C can be attributed to the evaporation of physically and chemically combined water in CSH [12,13]. Whereas, the endothermic peaks at about 450 °C are due to the decomposition of calcium hydroxide (CH). Obviously, the endothermic peaks of the decomposition of CH and CSH in the presence of GBFS and MK wastes are less than those of the control mix. This indicates that the presence of 30% GBFS and MK consumed the CH formed as a result of the hydration of OPC (pozzolanic reaction). Such an observation supports the results of X-ray diffraction analysis. In addition, the TGA curves can give quantitative information about loss in weight with increasing temperature. The total loss in weight by heating up to 900 °C in the presence of 30% GBFS and MK (MIII) is less than that in control mix. This result is in a good agreement with that of the combined water content. Therefore, the presence of both GBFS and MK cause a decrease in the combined water content.

Potential measurement (corrosion detection)

The results of the half-cell potential tests showed a tendency to decrease the potential readings with the time. The potentials obtained under humidity condition and in 3.5% NaCl solution

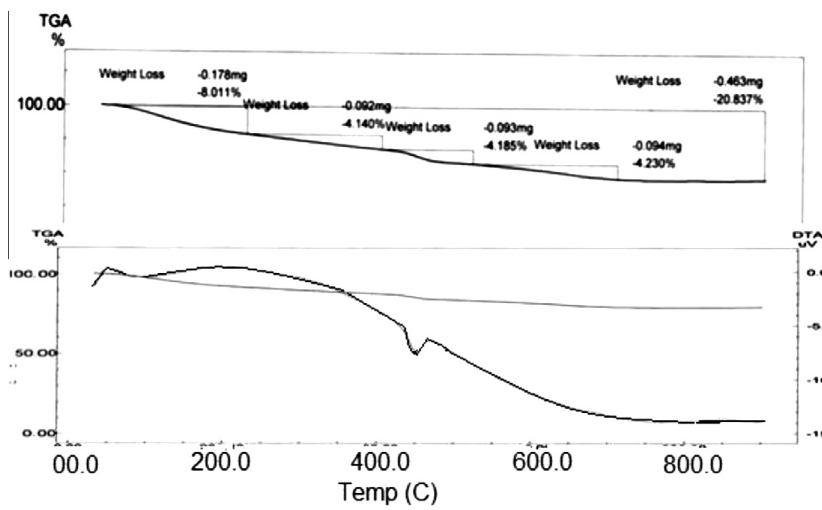

Fig. 6 TGA and DTA curves for control mix (Mo) at 28 days of hydration.

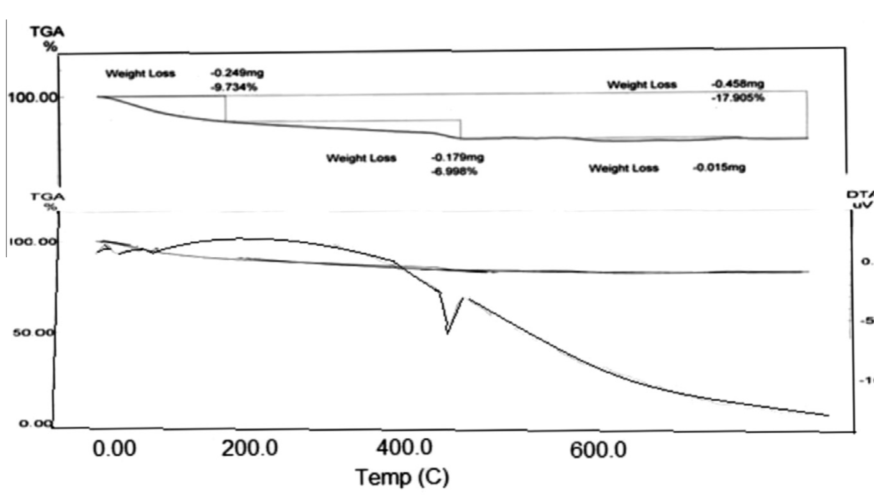

Fig. 7 TGA and DTA curves for 30% GBFS and Mk (MIII) cement pastes at 28 days.

Table 2 Potential readings of reinforced steel, with different granulated furnace slag–metakaolin.

Time (days)	Potential reading (mV)			
	Slag–metakaolin–cement ratios			
	0/0/100	5/5/90	10/10/80	15/15/70
0	−4	−121	−125	−137
10	6	−97	−102	−122
20	19	−55	−79	−98
30	22	3	−36	−24
40	51	3	−8	−28
50	73	7	3	−22
60	86	10	6	−20

Table 3 Potential readings of reinforced steel, with different granulated furnace slag–metakaolin–cement pastes, immersed in 3.5% NaCl solution.

Time (days)	Potential reading (mV)			
	Slag–metakaolin–cement ratios			
	0/0/100	5/5/90	10/10/80	15/15/70
0	150	103	78	62
10	158	112	128	64
20	189	146	145	89
30	233	198	175	118
40	230	203	189	145
50	249	236	213	173
60	258	236	218	172

falls within the range of accepted passive condition. The high corrosion potentials in the slag–metakaolin–cement paste specimens may be attributed to reducing effects of sulfur species derived from slag. These sulfur species can reduce the potentials depending on the paste environment. However, the corrosion rate remains low. The higher potential was measured for higher slag–metakaolin content; this means that the mineral admixture (slag–metakaolin) can reduce the probability of steel corrosion in pastes. Comparing the results of Tables 2 and 3, it is observed that, a more effective barrier film against further corrosion of the steel rod was observed under humidity conditions rather than that in 3.5% NaCl solution. This could be attributed to the continuous diffusion of chlorine ions through the paste and depassivating the protective layer on the reinforcement steel. Such observation is in agreement with the previous studies [14,15].

Conclusion

The main conclusions derived from this investigation are summarized as follows:

(1) For all cement blends, increasing metakaolin–slag contents in the range used in this investigation decreases the chemically combined water content and increases the compressive strength values.
(2) XRD showed a decrease in the intensity of CH peaks in the presence of MK and GBFS.
(3) The electrical conductivity values for all the investigated specimens are increased during the first few minutes of hydration and then decreases with time.
(4) Thermal analysis confirmed the results of X-ray diffraction analysis and combined water content.
(5) The specimens with higher slag–metakaolin contents were found to have higher resistance to corrosion; this means that the mineral admixture (slag–metakaolin) can reduce the probability of steel corrosion in concrete structures.

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